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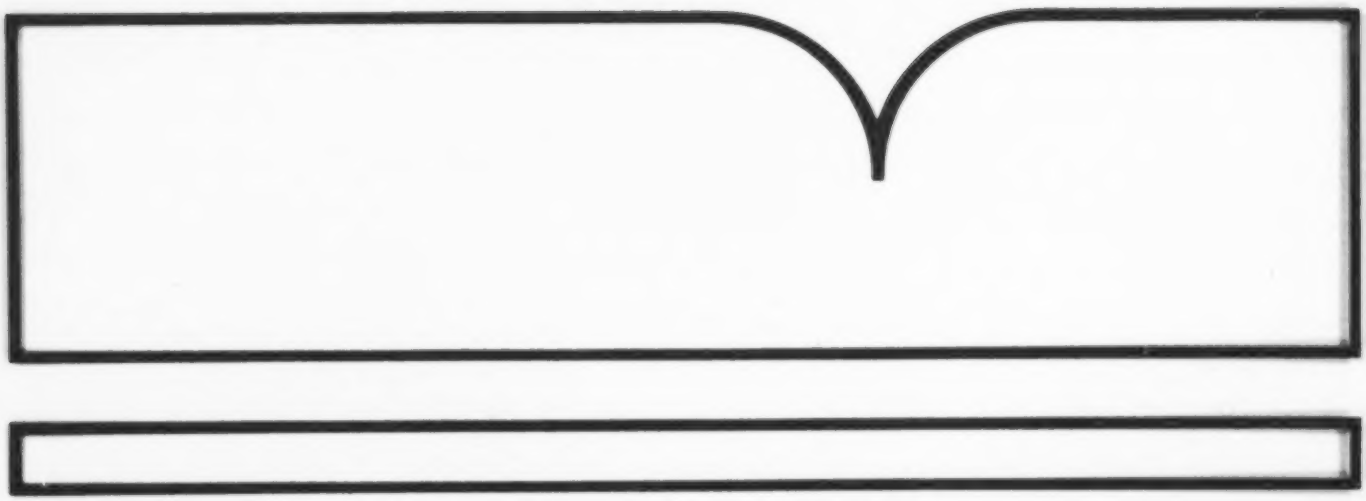

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M. L. Wesely, D. R. Cook, and R. L. Hart

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16. ABSTRACT

Eddy-correlation measurements of the vertical fluxes of ozone, carbon dioxide, fine particles with diameter near 0.1 μm, and particulate sulfur, as well as of momentum, heat and water vapor, have been taken above a tall leafless deciduous forest in wintertime. During the experimental period of one week, ozone deposition velocities vary from about 0.1 cm s^{-1} at night to more than 0.4 cm s^{-1} during the daytime, with the largest variations associated primarily with changes in solar irradiation. Carbon dioxide fluxes are directed upward, due to respiration in the leaf litter and soil beneath the canopy, and exhibit a strong dependence on air temperature. The fluxes are approximately zero at air temperatures less than 5 C and approach 0.8 mg m^{-2} s^{-1} when temperatures exceed 15 C during the daytime. Fine-particle deposition rates are large at times, with deposition velocities near 0.8 cm s^{-1} when turbulence levels are high, but fluxes directed upward are measured above the canopy when the surface beneath is covered with snow. Deposition velocities for particulate sulfur are highly variable and average to a value small in magnitude as compared to similar measurements taken previously over a pine forest in summer.

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FLUXES OF GASES AND PARTICLES ABOVE A DECIDUOUS FOREST IN WINTERTIME

M. L. WESELY, D. R. COOK, and R. L. HART

Atmospheric Physics Section, Environmental Research Division, Argonne National Laboratory, Argonne, IL 60439, U.S.A.

(Received in final form 23 September, 1983)

Abstract. Eddy-correlation measurements of the vertical fluxes of ozone, carbon dioxide, fine particles with diameter near 0.1 μm, and particulate sulfur, as well as of momentum, heat and water vapor, have been taken above a tall leafless deciduous forest in wintertime. During the experimental period of one week, ozone deposition velocities varied from about 0.1 cm s^{-1} at night to more than 0.4 cm s^{-1} during the daytime, with the largest variations associated primarily with changes in solar irradiation. Most of the ozone removal took place in the upper canopy. Carbon dioxide fluxes were directed upward due to respiration and exhibited a strong dependence on air temperature and solar heating. The fluxes were approximately zero at air temperatures less than 5 °C and approached 0.8 mg m^{-2} s^{-1} when temperatures exceeded 15 °C during the daytime. Fine-particle deposition rates were large at times, with deposition velocities near 0.8 cm s^{-1} when turbulence levels were high, but fluxes directed upward were found above the canopy when the surface beneath was covered with snow. Diffusional processes seemed to dominate fine-particle transfer across quasilaminar layers and subsequent deposition to the upper canopy. Deposition velocities for particulate sulfur were highly variable and averaged to a value small in magnitude as compared to similar measurements taken previously over a pine forest in summer.

1. Introduction

Experimental studies of the exchange of many trace substances between the atmosphere and cold wintertime landscapes are rare relative to the frequency of efforts during warm conditions. In winter, however, surface deposition delivers a dose that can be felt by living organisms later during warm weather. A well-known example is the possible buildup of acidic chemicals deposited on snow that later might be released to harm biota in waters that receive the snowmelt. Concerns over such suspected effects have led to studies designed to measure the 'dry' deposition, i.e., that not aided by precipitation, of gaseous and particulate sulfur to snow (e.g., Whelpdale and Shaw, 1974; Dovland and Eliasson, 1976; Barrie and Walmsley, 1978; Ibrahim *et al.*, 1983). There are many other substances that undergo air-surface exchange worthy of study. The wintertime air-surface exchange of carbon dioxide, for one, indicates rates of respiration by microorganisms breaking down organic material and thus releasing stored carbon during cold seasons. Another gas, ozone, causes weathering of many surface materials during removal from the atmosphere and is prominent in atmospheric chemical reactions involving oxidation of some pollutant gases to form particulate material.

The study of air-surface exchange involves subsets of several scientific disciplines, usually including micrometeorology. This paper examines the results of an experiment that utilizes the micrometeorological method of eddy correlation to measure net vertical fluxes. This is a proven technique when applied within certain limitations. For this

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experiment, the vertical fluxes of ozone, carbon dioxide, fine particles, and particulate sulfur were measured above a leafless wintertime deciduous forest, over a period of approximately one week. While the observations were limited to one time period and location, the data are rather unique for this type of highly prevalent surface. Indeed, examination of recent review articles (e.g., McMahon and Denison, 1979; Sehmel, 1980) leads to the conclusion that measurements of gas and fine particle deposition to such a wintertime surface in the field are quite rare. Hence, this paper provides an important building block in the understanding of processes of air-surface exchange.

Micrometeorological techniques such as eddy correlation applied above the surface provide a means to measure net vertical fluxes in the lower atmosphere, but do not give direct information on chemical and physical processes at the surface that can strongly affect the fluxes aloft. The several substances measured in this experiment, however, have widely different properties and thus different causes of air-surface exchange. As will be shown, these differences aid interpretation of results with regard to where crucial processes of exchange are found in the leafless canopy and underlying surface.

2. Methods

Measurements were taken from January 25 to February 1, 1981, above a mixed stand of oak, hickory, and tulip poplar trees located in the Blackwood Division of the Duke Forest and about 15 km west of Durham, North Carolina, U.S.A. The upper branches of the trees extended to an average of approximately 28 m above the local soil surface, and the trees had no leaves except on a few scattered coniferous trees in the distance. The eddy-correlation instruments were deployed from a scaffold tower at a height of about 39 m above the soil surface.

A suite of eight fast-response eddy-correlation instruments was employed successfully. The ozone concentrations were measured with a chemiluminescent device described by Wesely *et al.* (1981) in conjunction with the same types of fast-response sensors for horizontal wind speed u, vertical wind speed w, air temperature T, and absolute humidity q. The sensor for measuring carbon dioxide concentration is the same as was used over ocean (Wesely *et al.*, 1982) and over an agricultural crop (Wesely, 1983). The fine particle sensor, used in numerous eddy-flux studies starting with that described by Wesely *et al.* (1977), is most sensitive to particles with diameters of approximately 0.05 to 0.1 μm and is not specific to chemical species. The device measures particle concentration as a number density with a slightly increasing sensitivity as the particle size increases. The particulate sulfur sensor used is a flame-photometric detector built at the University of Michigan at Ann Arbor. It actually measures the total sulfur concentration, gaseous plus particulate, similar in operation to the commercially-available flame-photometric sensor used by Hicks *et al.* (1982), but here with the gaseous sulfur removed by use of a denuder tube on the inlet. This tube is a simple glass tube 25 cm long coated with sodium carbonate on the inside. Because of deposition of the large and very small particles on the long inlet tube that was attached to the sulfur sensor, the size range of the particles detected is probably confined within 0.01 to 2 μm diameter.

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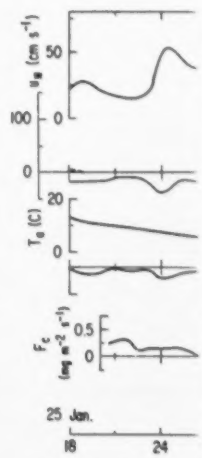

Fig. 1. A sample of some

Samples of the concentration of ozone (o), carbon dioxide (c), fine particles (p), and submicron particulate sulfur (s) were all brought from near the vertical wind sensor to their respective sensors through tubing that ranged from 1 to 3 m long and with flow velocities different for each instrument. The resulting time lags between the concentration and vertical velocity signals were effectively eliminated during analysis by adjusting the digital time series of the signals generated. Further analysis of the data to produce the eddy-correlation flux estimates included high-pass filtering to remove trends lasting longer than 200 s and corrections computed to compensate for the relatively slow response of some of the sensors, as described by Wesely (1983) and the papers referred to therein. Ultimately, the deposition velocity v_d or the normalized flux $F_\chi/\overline{\chi}$ of a species of a mass or particle number density χ at the height of measurement was computed as

$$v_d \equiv -F_\chi/\overline{\chi} = -\overline{w'\chi'}/\overline{\chi} - W, \qquad (1)$$

where F_χ is the flux computed for one-half hour, w is the vertical wind velocity, overbars indicate half-hour means, and primes specify deviations from means over approximately 200 s. Also, W represents an adjustment to account for density fluctuations at the point of measurement and for Stefan flow associated with vertical water vapor flux (Webb *et al.*, 1980; Wesely *et al.*, 1981). The adjustments for the effects of Stefan flow were very small and were neglected when no data on water vapor flux were available.

Figure 1 is an illustration of the type of information obtained during 2–3 days of the experiment. In all cases, half-hour averages of the fluxes were obtained; these form the primary data set. The curves in Figure 1 result from a considerable amount of subjective hand-smoothing and interpolation and thus should not be used to obtain precise values of the fluxes. No snow was present for the times shown in Figure 1 and, as indicated

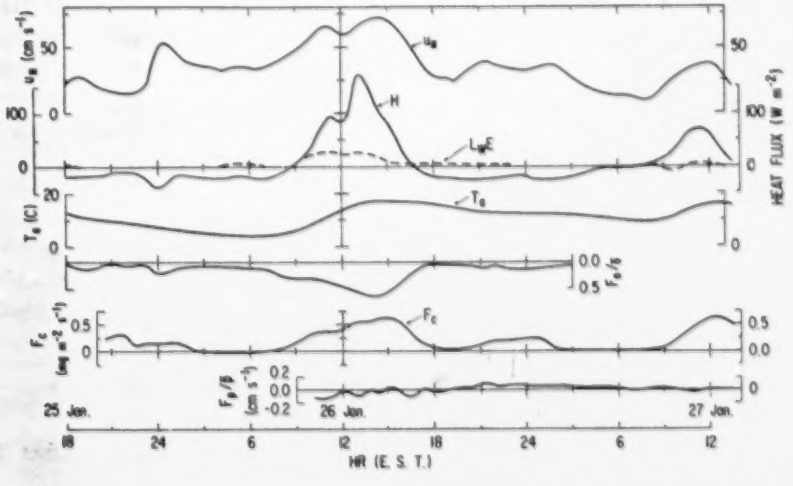

Fig. 1. A sample of some of the measurements obtained on January 25–27, indicated by hand-drawn smoothed curves.

in the figure, air temperature T_a at a height of 42 m varied from 5 to 16 °C. Strong diurnal variations of the eddy-correlation estimates of friction velocity u_*, sensible heat flux H, ozone flux F_o, and carbon dioxide flux F_c are evident. The flux $L_w E$ of latent heat was measured only intermittently during the experiment and was always quite small in absolute value. On some occasions other than shown in Figure 1, the magnitude of the flux F_p of fine particles was quite large. The flux of particulate sulfur was measured on only a few occasions and will be considered in detail later in the paper.

Figure 1 shows ozone and particle vertical transfer rates expressed as normalized flux instead of its negative, the deposition velocity v_d, in order to preserve the convention of a positive sign indicating scalar fluxes being directed upward, away from the surface, and a negative sign for downward atmospheric transfer. In most of the remainder of this paper, use of deposition velocities will be preferred.

Table I summarizes conditions during the entire experiment. Normal diurnal cycles of mean wind speed $\bar{u}$ and air temperature T_a, both measured at a height of 42 m, were encountered in most cases. When wind speeds were less than 1.0 m s^{-1} at the 42 m height, the data were usually discarded because weak winds usually do not properly drive the mechanical eddy-correlation wind sensors used. This, together with no sampling during precipitation, accounts for the lack of data during most of the time periods missing in Table I. A few particularly notable events occurred during the week of measurements. Winds became quite gusty on the night of January 29–30, with the approach of a snow storm. The associated cold-air advection resulted in the sensible heat flux being directed upward, opposite to the usual direction at night. On the following two days, snow covered the leaf litter and soil beneath the canopy. With melting snow on the ground on February 1, the sensible heat fluxes were directed downward during the daytime, again a feature opposite to the usual situation.

TABLE I

General aspects of experimental conditions. Slightly unstable atmospheric conditions are indicated by 's. unstable', and usually refer to cases when the sensible heat fluxes were between 0 and 50 W m^{-2}

Day 1981 Jan.–Feb.		$\bar{u}$ (m s^{-1})	Atmospheric stability	T_a (°C)	Notable events
25–26	night	2.5–3.5	stable	5–10	frost
26	day	3.5–6.0	unstable	8–16	strong winds
26–27	night	1.5–3.5	stable	9–15	no frost
27	day	2.0–2.5	s. unstable	10–15	rain after 1330
28	day	1.0–4.0	unstable	7–10	no morning frost variable wind dir.
29	day	3.5–5.5	unstable	7–15	morning frost strong winds
29–30	night	2.5–5.5	s. unstable	−2 to 10	variable wind dir.
30–31	night	2.0–3.0	stable	−3 to −7	~10 cm snow
31	day	1.5–3.0	stable	0 to −2	~10 cm snow
1	day	1.5–4.5	stable	3–10	melting snow

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Interpretation of deposition velocities over the tall leafless deciduous forest is more difficult than in many past studies conducted over surfaces with much shorter surface elements. An approach often used to study deposition processes above short canopies or nonvegetated surfaces is to consider resistance to vertical transport across horizontal layers of air and canopy; the physical bounds of the layers are often more conceptual than actual, especially for layers located within the canopy. In this way, the deposition velocity can be expressed as

$$|v_d| = (r_a + r_s + r_c)^{-1}, \tag{2}$$

where the absolute value is taken in order to accommodate fluxes directed upward as well as downward and still avoid the mathematical generation of a negative resistance. The aerodynamic resistance r_a applies between the point of measurement and the top of the canopy; r_s is a composite gas-phase resistance within the canopy and usually only concerns transfer across the quasilaminar sublayers that envelop surface elements; and r_c is the bulk resistance of surface materials to retaining or releasing the trace substance. Ordinarily, the main objective of employing Equation (2) is to calculate estimates of the surface resistances r_c and sometimes r_s; r_s can be calculated for gases (e.g., Wesely and Hicks, 1977) but remains one of the unknowns in particle transfer processes. The value of r_a can be calculated from known flux-gradient relationships that depend on estimates of friction velocity u_*, atmospheric stability, height above the surface, pollutant uptake displacement height, and surface roughness length (e.g., Wesely and Hicks, 1977). For the leafless deciduous forest, however, the information on the displacement height and its relationship to sources and sinks in the canopy is insufficient to allow accurate calculations of r_a and even to determine whether the form of Equation (2) is adequate. This is a well-known problem in micrometeorological studies above forests (Tajchman, 1981), and the absence of leaves increases the difficulty because of decreased capture or release efficiency of the upper canopy. In some cases, the majority of the transfer might originate at the ground beneath the canopy. Nevertheless, some information on surface resistances can be gained by consideration of the aerodynamic resistance to vertical momentum flux. If most of the air-surface exchange of the substances takes place in the upper canopy, then the bulk surface resistance given as $(r_s + r_c)$ can be approximated as $|v_d^{-1}| - V/u_*^2$, where V is the mean horizontal wind speed and the effect of atmospheric stability is ignored (e.g., Hicks *et al.*, 1982). The range of V/u_*^2 is 0.09 to 0.15 s cm^{-1} for the data reported in this paper. Since these resistances are usually quite small compared to the value of $|v_d^{-1}|$ found, the latter is most often only a slight overestimate of the bulk surface resistance.

3. Results and Discussion

3.1. Ozone

Table II summarizes the results on ozone deposition velocities $v_d = -F_o/\bar{o}$, where $\bar{o}$ is the mean ozone concentration during the half-hour measurement periods. Ozone con-

TABLE II

Averages of ozone deposition velocities for the number of half-hour samples obtained during the time intervals shown. The error bounds on v_d indicate standard errors.

Day 1981 Jan.–Feb.	Time (EST)	No. samples	v_d (cm s^{-1})
25	12:30–17:00	4	0.23 ± 0.12
25–26	17:30–09:00	20	0.11 ± 0.02
26	09:00–17:00	8	0.38 ± 0.08
26–27	17:30–03:00	16	0.11 ± 0.01
27	12:00–13:30	3	0.18
28	13:00–17:00	6	0.26 ± 0.05
29	08:30–17:00	16	0.27 ± 0.03
29	17:00–23:00	11	0.11 ± 0.06
31	10:00–12:00	4	0.38 ± 0.14
1	10:30–15:00	8	0.45 ± 0.09

centrations varied from 1 to 6 ppbv. These results have already been described (Wesely, 1983), except that the nighttime deposition velocities reported here are slightly larger (0.11 versus 0.06 cm s^{-1}) as a result of closer examination of the data. Primarily, the increase resulted from discarding data obtained during very small wind speeds, less than 1.0 m s^{-1}, when the mechanical vertical wind sensor might not have responded accurately. Some increase also resulted from more thorough data processing, correcting for inadequate sensor frequency responses, especially for data collected in stable conditions.

Daytime O_3 deposition velocities range from 0.23 to 0.45 cm s^{-1}, not considering the value of 0.18 cm s^{-1} obtained on January 27. The latter day had heavily overcast skies and might represent conditions intermediate between daytime and nighttime. These daytime values are smaller than suggested for summertime forests on the basis of analogy to water vapor transfer (e.g., Wesely and Hicks, 1977; Galbally and Roy, 1980) or by direct measurement (Lenschow *et al.*, 1982; Hicks *et al.*, 1982), which is not surprising because of the absence of leaves for air-surface exchange through leaf stomata, or small pores, by which plants release water vapor and oxygen while taking up carbon dioxide.

The average nighttime ozone v_d is 0.11 cm s^{-1} which is very close to that found over a pine forest in summer at night when leaf stomata were closed (Hicks *et al.*, 1982), but considerably smaller than found in numerous studies for short vegetative canopies at night (as reviewed by Wesely, 1983). Apparently, tall canopies often block transport to the surfaces beneath, and most of the O_3 destruction takes place on the abundant, but fairly inert, nighttime canopy surfaces.

With the absence of photosynthesizing surfaces in the leafless deciduous forest, a major question is why there is such a large change in ozone v_d from day to night. Despite the subfreezing temperatures during the daytime of January 31, for example, the deposition velocities are as large as on other days when it was warmer (temperatures are indicated in Table I). This rules out a significant influence of biological activity,

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which would be modulated by temperature, and any other effect of temperature changes such as once suggested by Galbally (1971). Another important consideration is that the snow on the surface beneath the canopy on January 31 and February 1 does not seem to have retarded O_3 deposition even though the surface resistance of snow to O_3 removal is quite large (Wesely *et al.*, 1981), probably much larger than for leaf litter exposed without snow present.

The small nighttime deposition velocities for O_3 being characteristic of tall canopies and the lack of an influence by snow present on the surface suggests that most of the O_3 destruction occurs on the exposed branches and twigs of the leafless forest canopy. However, the destruction rate does not seem to be dependent on wind speed or friction velocity u_*, which should influence the amount of mixing downward into the canopy. A similar influence might ordinarily be related to atmospheric instability, but the small values of v_d on the night of January 29–30 during slightly unstable conditions compared to the large values on the day of February 1 with stable conditions indicates that atmospheric stability plays a minor role. Of course, with extremely stable conditions, the magnitudes of all vertical fluxes become quite small because the aerodynamic resistance to vertical transport above the canopy becomes excessively large; we are ignoring such a situation in this analysis. We are left with a situation where O_3 removal seems to take place in the upper canopy and increased atmospheric mixing does not seem to enhance removal deep in the canopy.

These observations of enhanced daytime O_3 surface removal above surfaces without active leaf stomata have also been observed by Wesely *et al.* (1978) for senescent maize and by Galbally and Roy (1980) for brown grass. It has been suggested that enhanced removal could be caused by photoactivation of surface receptor sites (Galbally and Roy, 1980) or by chemical or photochemical reactions in the air beneath the point flux measurement (e.g., Lenschow *et al.*, 1982). It is beyond the scope of this paper to consider fully all the possibilities, but it is worth noting that the present observations would support the contention that the O_3 destruction rate beneath the point of measurement is somehow modulated directly by solar radiation. Indeed, solar irradiation of the upper canopy probably increased on January 1 and February 31 because of reflection by snow on the surface, and this is correlated with relatively large deposition velocities on those days. Increased solar radiation would certainly warm surfaces and thus might cause emission of reactive gases, would enhance transfer to warmed surfaces in the canopy by inducing very local improved mixing, and would provide for photoactivation of receptor sites. The effect of warming on gas emissions, however, seems inconsequential in consideration of the low air temperatures on certain days. Further, the enhancement of mixing from individual warmed surfaces greatly beyond that expected on the basis of known theory in turbulent transfer seems unlikely. More research is clearly needed on photochemical reactions in the air and on surfaces exposed to O_3.

For the present we shall assume that a typical value of $(r_a + r_s)$ for gases to the upper canopy is approximately 0.2 s cm^{-1}. Then r_c can be estimated approximately as $(v_d^{-1} - 0.2)$. According to Table I, then, r_c can be estimated on the basis of total solar irradiation T as

$$r_c \approx \begin{cases} 9\ \text{s cm}^{-1} & T = 0 \\ 5\ \text{s cm}^{-1} & \text{small } T \\ 3\ \text{s cm}^{-1} & \text{moderate } T \\ 2\ \text{s cm}^{-1} & \text{large } T, \end{cases} \tag{3}$$

where $T = 300$–$450\ \text{W m}^{-2}$ is typical for midday solar irradiation on a horizontal surface at the experiment site and corresponds to a 'moderate' value of T. A quantity more relevant then T might be just the ultraviolet component of the solar radiation, if photochemical reactions were involved. Although the value of $r_c = 2$–$3\ \text{s cm}^{-1}$ is near that found by Wesely *et al.* (1978) for senescent maize during the daytime, the agreement might be fortuitous. That is, the maize canopy was degrading and thus probably was more effective in removing ozone, while the O_3 concentrations were nearly ten times greater than above the deciduous forest.

3.2. Carbon dioxide

The flux F_c of carbon dioxide over the leafless deciduous forest was almost always directed upward, indicating respiration by tree roots, microorganisms in the leaf litter and soil, and above-ground tree boles, branches and twigs. Inspection of data for the afternoon of January 26 in Figure 1 reveals that F_c seems to increase as sensible heat flux and friction velocity increase, which might indicate that the vertical transfer deep in the canopy is limited by aerodynamic resistances. Indeed, in reference to the discussion above on the O_3 deposition velocities, the aerodynamic resistances beneath the upper canopy seem to be large, large enough to prevent significant O_3 destruction at the leaf litter surface for all atmospheric conditions; visual observations of the lack of wind-induced flutter of solitary brown leaves near the forest floor indicated that turbulent mixing was very weak near the ground. However, it is unlikely that large aerodynamic resistances near the ground would slow the emission of CO_2 from the lower canopy, litter and soil (including roots). Carbon dioxide might accumulate near the surface materials beneath the upper canopy, eventually to be slowly ventilated to the atmosphere above the canopy when a very small amount of wind-induced mixing occurs or when solar heating deep in the canopy produces convective mixing. In this case the physical meaning normally ascribed to surface resistance r_s and r_c and in Equation (2) would not be appropriate. Instead, another aerodynamic resistance r_{ac} for the region beneath the uppermost canopy would have to be specified, as well as a resistance r_f for the forest floor. Equation (2) might then be replaced with:

$$F_c/\bar{c} = r_a + r_x, \tag{4a}$$

where

$$r_x = [(r_{ac} + r_f)^{-1} + r_b^{-1}]^{-1}. \tag{4b}$$

Here, we have used the expedient of identifying a single parallel resistance r_b for CO_2 release from boles, branches and twigs; this includes both aerodynamic and physiological

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Figure 2 of CO_2 flux on

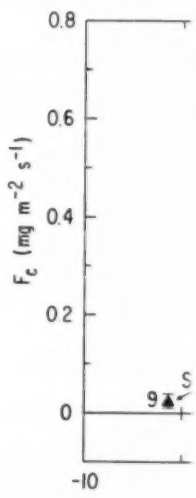

Fig. 2. Carbon dioxide fluxes
are greater than 50 W m^{-2} (●)
samples whose number is giv
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series resistances somehow distributed vertically over the same region where r_{ac} is found.

The temperature of surface materials seems to affect respiration directly. This is to be expected because it is well known that the rate of enzymatic reactions involved in respiration increases rapidly with rising temperature, approximately doubling for every 10 °C increase of temperature. Figure 2 shows the variation of F_c with air temperature measured at a height of 42 m, about 14 m above the forest canopy. The data point at 1.8 °C was taken between midnight and 03 : 30 hr on January 30 when no snow covered the ground and the point at − 1.8 °C is for 03 : 30 to 09 : 30 hr when a very light dusting of snowfall was occurring. The nearly zero values of F_c on these occasions support the contention that low temperatures can effectively shut off the release of CO_2, and thus make r_f and r_b very large. As would be expected because of the added physical barrier to CO_2 release from soil and litter, small fluxes are also found with a substantial snow cover. At greater temperatures, the upward flux of CO_2 increases, to values exceeding maximum values near 0.5 mg m^{-2} s^{-1} estimated by others for emission from various surfaces. These include, for example, flux from soil under a wheat crop at midday (Denmead, 1976), the net exchange beneath the upper levels of a tropical rain forest canopy (Allen and Lemon, 1976), total canopy and surface respiration in a Sitka spruce forest (Jarvis *et al.*, 1976), and nighttime release of CO_2 from an entire stand of oak trees 10 m tall (Woodwell and Dykeman, 1966). There is also an obvious dependence in Figure 2 of CO_2 flux on sensible heat flux. The large heat fluxes indicated by Figure 2

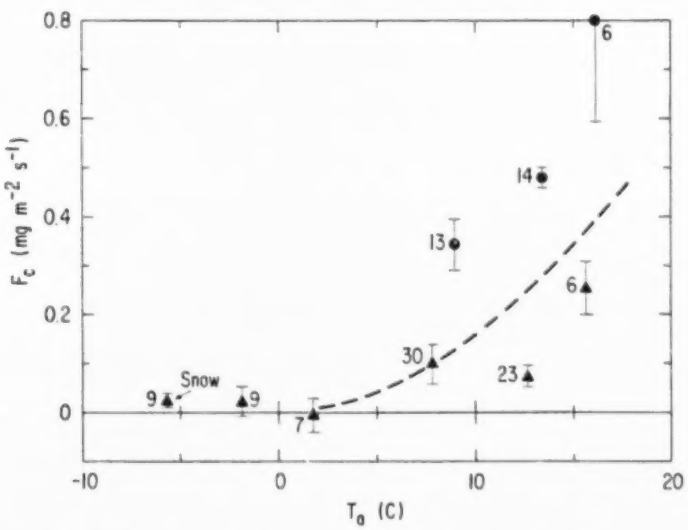

Fig. 2. Carbon dioxide fluxes versus air temperature above the canopy for cases when sensible heat fluxes are greater than 50 W m^{-2} (●) and when less (▲). Error bars indicate standard deviations on the half-hour samples whose number is given by each point. The dashed curve represents an empirical subjective evaluation for atmospherically near-neutral conditions.

only occur with clear daytime skies, when solar irradiation is large. Thus the increase of F_c might be associated with temperatures of surfaces within and beneath the canopy being considerably greater than T_a. Likewise, radiational cooling at night would depress surface temperatures substantially below the air temperature. Unfortunately, no measurements of the temperature of leaf litter or other surfaces were taken during this experiment.

The dashed curve drawn in Figure 2 represents the equation

$$F_c = 0.0015T_a^2, \tag{5}$$

where T_a is expressed in deg C. This curve is partly based on measurements taken during near-neutral conditions, when surface temperatures would be quite close to the temperature above the canopy, and is an attempt to ascribe all the variation to changes in r_f and r_b in Equation (4). But due to the sparseness of such data, Equation (5) should be considered as only a subjective evaluation meant merely to indicate the general nature of the appearance of such a curve. The choice of an exponential value of 2 for T_a is somewhat arbitrary and follows preconceived notions on the form of nonlinearity being quadratic, as found by Edwards (1975) for example. The curve given by Equation (5) roughly weights the data taken during atmospherically stable conditions twice as much as the data from unstable conditions, thus approximately reflecting the proportions of the number of hours each of the two conditions should occur during the winter at the latitude of the experiment site.

It is noteworthy that the fluxes depicted in Figure 2 are nearly three times the values found for CO_2 evolution rates from the floor of a mixed deciduous forest, at a given temperature (Edwards, 1975). Also, the rather strong dependence on air temperature and surface heating from half hour to half hour as suggested by Figure 2 implies that peak CO_2 fluxes are most often found during the daytime, such as shown in Figure 1. This is opposite the usual trend found for soil (including roots) and tree bole respiration rates (e.g., Edwards and McLaughlin, 1978). Further research is needed to evaluate these differing results. For example, it is unknown how the rather thick leaf litter at the Duke forest compares as a source of CO_2 relative to other studies. Another unknown is the extent of CO_2 loss from branches and twigs as a function of their temperature.

3.3. Fine particles

Field measurements of the flux of fine particles with diameters near 0.05–0.1 μm have led to some rather ambiguous results in the past. The data by Hicks *et al.* (1982) typifies this situation in that fluxes are often directed upward, away from the surface, over vegetated surfaces at night and in the morning but are strongly directed downward in the afternoon. Over wet smooth surfaces, fluxes measured with this same fine-particle sensor give fluxes always directed upward (Wesely and Hicks, 1979). Garland and Cox (1982) find small deposition velocities above grass for particles in the appropriate size range, and possible upward fluxes intermittently. One possible explanation for the fluxes being directed upward is associated with humidity gradients. That is, the fine particles grow rapidly, though little in extent, when subjected to greater relative humidities,

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Table III gives t
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Averages of deposition
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Day 1981 Jan.–Feb.	Time (EST)
26	10:00
26–27	17:00
27	10:00
28	10:00
29	08:30
29–30	17:00
30–31	21:00
1	10:00

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especially at the relative humidities greater than 95% found very near wet surfaces. The particles might grow into a size range where they produce a slightly greater response in the sensor. Above wet surfaces, the updrafts would usually have a greater humidity than the downdrafts, as a result of the locations where the transported air parcels originate. This would cause an upward flux to be measured by eddy correlation, even though the small particles might not actually be emitted by the surface materials below.

Table III gives the half-day averaged deposition velocities $v_d = -F_p/\bar{p}$ for the fine particles. Strong upward fluxes are seen when the leaf litter is covered with snow on January 30–31, again suggesting some effect primarily associated with large relative humidities near the surface.

TABLE III

Averages of deposition velocities for fine particles and some simultaneously measured quantities for the number of half-hour samples obtained during the time intervals shown. Error bounds indicate standard errors.

Day 1981 Jan.–Feb.	Time (EST)	No. samples	v_d (cm s^{-1})	u_* (cm s^{-1})	$\sigma_\theta \bar{u}$ (cm s^{-1})
26	10:00–17:00	12	0.08 ± 0.05	60 ± 2	119 ± 8
26–27	17:00–09:00	20	−0.03 ± 0.01	28 ± 2	37 ± 3
27	10:00–13:30	6	−0.01 ± 0.004	54 ± 3	58 ± 6
28	10:00–17:00	10	0.34 ± 0.11	47 ± 7	125 ± 21
29	08:30–17:00	16	0.40 ± 0.16	61 ± 5	123 ± 10
29–30	17:00–08:00	28	0.43 ± 0.07	58 ± 5	302 ± 31
30–31	21:00–09:00	9	−0.25 ± 0.05	12 ± 2	46 ± 17
1	10:00–13:30	6	−0.41 ± 0.20	66 ± 5	129 ± 4

The case of upward fluxes of particles being measured above snow might be similar to the situation involving CO_2 transfer. That is, the effects of an apparent source of material at or very close to the ground will eventually be seen as an upward flux above the canopy; a large aerodynamic resistance below the upper canopy impedes the vertical transfer but does not prevent it from occurring. In such a situation, a fairly large increase in fine-particle and CO_2 concentration should occur close to the ground. Measurements to test for this increase were not taken in the present experiment, but such a situation for CO_2 in forests has been found in the past (e.g., Allen and Lemon, 1976).

We will ignore the effects of humidity gradients in the remainder of this analysis and consider only the cases without snow, when the effects evidently are not strong. Most fairly general treatments of fine-particle deposition over dry surfaces consider the processes of (1) diffusion, (2) interception, and (3) impaction of the particles on surface elements (e.g., Slinn, 1982). Then r_s in Equation (2) consists of three parts, namely,

$$r_s = (r_1^{-1} + r_2^{-1} + r_3^{-1})^{-1}, \tag{6}$$

where it has been assumed that parallel noninteractive pathways are represented by r_1, r_2, and r_3. The term r_c in Equation (2) would represent the effects of bounceoff and

resuspension, here neglected. The resistance r_3 to deposition by impaction is conventionally known to be very large unless particles significantly larger than 0.1 μm in diameter are considered and the impaction surfaces are considerably smaller than the twigs and branches of trees (e.g., Chamberlain, 1975). The process of interception is fairly well understood (e.g., Friedlander, 1977), and only a few calculations are needed to show that it is negligible for the present study, at least relative to the deposition velocities shown in Table III. Indeed, the absence of fine structures such as leaf hairs on the canopy makes the possibilities of deposition by interception and impaction very small.

The remaining term in Equation (6), that dealing with diffusion, needs to be seriously considered. Particles of radius 0.05 μm have a Brownian diffusivity near $D_p = 2 \times 10^{-5}$ cm^2 s^{-1} (Friedlander, 1977), which is nearly a factor of 10^4 smaller than the eddy diffusivity D_H for heat or water vapor. In conventional scaling arguments, this factor ($D_H/D_p \approx 10^4$) should be raised to the power $n = 1/2$ to $2/3$ to express the ratios of sublayer resistance for particles as compared to that for heat or water vapor. Specifically, Wesely and Hicks (1977) suggest that the resistance for this type of canopy would be that ratio multiplied by $a(ku_*)^{-1}$ where $a \approx 2$ is a numerical constant and $k = 0.4$ is the von Karman constant. Two recommendations by Brutsaert (1979) will be adopted here. Namely, the value of $a \approx 1$ seems most appropriate for forests and the exponent n should be small, near 0.5, for turbulent flow over dense vegetation. Then, the bulk resistance r_s becomes

$$r_s \approx r_1 \approx (ku_*)^{-1}(D_H/D_p)^{1/2}, \tag{7}$$

which for the present case becomes

$$r_s \approx 250u_*^{-1}. \tag{8}$$

Although the values of v_d in Table III are highly scattered with regard to u_*, an average of all data produces values of u_*/v_d near 210, where $r_s = v_d^{-1}$ has been assumed, quite close to 250 suggested in Equation (8). In contrast, values of $u_* r_s$ measured with the same instrumentation over a pine forest in the afternoon (Hicks *et al.*, 1982) are typically near 60. This suggests that diffusion is the major process of transfer for fine particles to the surfaces of the leafless forest, but that other processes such as impaction and interception of fine particles might be important in the pine forest. Clearly, there was much more surface area available for interception at the pine forest, but even an order of magnitude increase in area would not increase deposition by interception to such a significant extent, according to arguments such as presented by Slinn (1982); likewise it is difficult to conceive of how impaction could be important for such small particles because of their extremely small stopping distance and thus great ability to follow the flow around obstacles.

The fact that there is a great deal of scatter in the relationship between u_* and v_d is disturbing. An analysis more thorough than presented in Table III indicates that v_d is nearly zero, on the average, for values of u_* less than 45 cm s^{-1}, while peak values of v_d are found near u_* equal to 70 cm s^{-1}. A significant correlation between v_d and $\sigma_\theta \bar{u}$

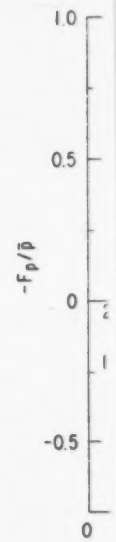

Fig. 3. Fine-particle d
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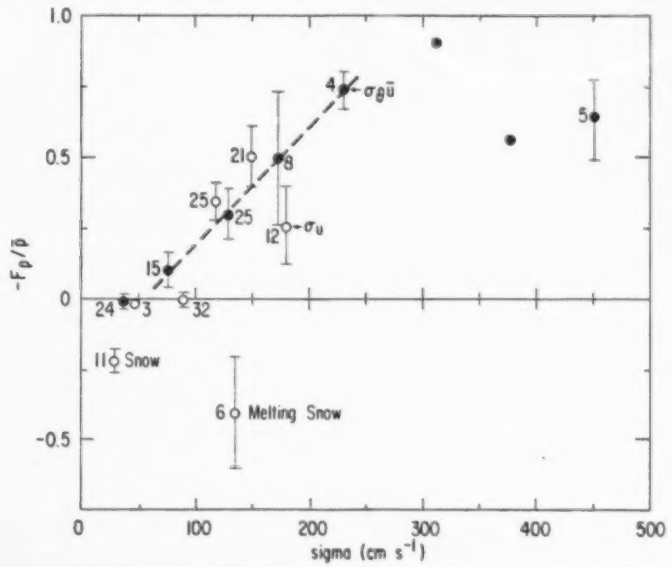

Fig. 3. Fine-particle deposition velocity versus $\sigma_\theta\bar{u}$ and σ_u, with standard errors shown for the number of half-hour samples given next to each point. No snow was present for all points other than those designated. The straight dash line was drawn by eye.

has been found, however, and this is shown in Figure 3. The σ_θ is the average standard deviation of horizontal wind direction for each half hour as measured with the use of a wind vane at a height of 42 m and calculated with 5-min running means. The wind vane used has a fairly slow response, so that the values of $\sigma_\theta\bar{u}$ are usually an underestimate of σ_v, the standard deviation of the crosswind component. Nevertheless, $\sigma_\theta\bar{u}$ becomes quite large at times, such as in the synoptically disturbed conditions on the night of January 29–30. The standard deviation σ_u of the horizontal wind fluctuations measured at 39 m with the fast-response cup anemometer used in eddy correlation does not show such large increases. This indicates that multiple horizontal wind direction shifts have trends not entirely removed by computation of σ_θ with 5-min means.

A nearly linear relationship is seen in Figure 3 for v_d of fine particles versus $\sigma_\theta\bar{u}$, up to values of near 200 cm s^{-1} for the latter. The correlation with σ_u (and u_*) is less well defined. With snow, the effect of a high-humidity surface is evident. For values of $\sigma_\theta\bar{u}$ exceeding 200 cm s^{-1}, v_d seems nearly constant, indicating that mean wind shifts have probably significantly contaminated the measurements of σ_θ and that v_d is not affected by the slow meandering motions. This helps to explain why v_d does not scale linearly with long-term averages of $\sigma_\theta\bar{u}$ when a few large values are included, which occurred on the day of January 26 and the night of January 29–30 in Table III.

As a result of the strong correlation of v_d with $\sigma_\theta\bar{u}$, it appears that a major feature of large levels of turbulence that is important in aiding deposition might be rapid changes

in wind direction (possibly in the vertical as well as in the horizontal plane since the magnitude of vertical wind variance often changes in a fashion similar to σ_v variations), in addition to speed fluctuations. Perhaps wind direction changes aid excessively in disrupting the quasilaminar sublayers on surface elements. This would cause motions in viscous boundary layers where even weak fluctuations can enhance particle transport significantly while producing little change in momentum flux or u_* (Friedlander, 1977).

3.4. Particulate Sulfur

Table IV gives the 19 half-hour values of v_d for particulate sulfur measured during the experiment, along with other variables. No correlation of this v_d with other variables is apparent, possibly as a result of the limited number of data points, the low concentrations of particulate sulfur encountered (mostly near 3 ppbv), and the low signal-to-noise ratio of the sulfur sensor output. Although the noise was random in the sense that it was not correlated with vertical wind speed, the noise can greatly increase the amount of run-to-run variability. The overall average v_d for particulate sulfur is -0.08 ± 0.18 cm s^{-1}, not a very satisfactory result because of the relatively large scatter. There is a slight increase on January 28 as compared to the earlier values, and this corresponds to greater values of $\sigma_\theta \bar{u}$ and v_d for fine particles, but the increase in sulfur v_d is not statistically significant. In general, results indicate a rather small magnitude of v_d for particulate sulfur, at least in comparison to values measured above a pine forest (Hicks *et al.*, 1982) and grass (unpublished work by the present authors).

The size range of the particles detected with the present sulfur sensing system is within 0.01 to 2 μm diameter, and most of the sulfur mass above the leafless deciduous forest was probably near the peak of accumulation size mode, typically at particle diameters of approximately 0.4 μm. As with the case for fine particles, we assume that most of the small-particle deposition would take place in the upper canopy, so that Equation (2) applies. We neglect bounceoff, so that r_c is approximately zero, and assume that r_a is much smaller than r_s. Also, the bulk interception resistance r_2 included in Equation (6) is assumed small. Our primary considerations for deposition velocity are expressed as:

$$v_d \approx r_s^{-1} \approx r_1^{-1} + r_3^{-1} . \tag{9}$$

According to arguments leading to Equation (7), the bulk resistance to diffusion across the quasilaminar sublayers, for particles of 0.4 μm diameter and thus with D_p approximately equal to 2.2×10^{-6} cm^{-2} s^{-1} (Friedlander, 1977), is

$$r_1 \approx 1000 u_*^{-1} . \tag{10}$$

This produces deposition velocities of 0.05 cm s^{-1} when u_* is 50 cm s^{-1}, a typical situation above forests for moderate wind speeds of approximately 4 m s^{-1} at a height of 10 m above the treetops. The resistance r_3 related to impaction will be discussed later.

While the present measurements of v_d for sulfate above the forest do not disagree with the predictions given by Equation (10), the scatter in the data is very large. Nevertheless, it is of interest to examine Equation (10) in comparison to other expressions available in the literature. Equation (10) results from the efforts of many scientists and is derived

TABLE IV

Summary of half-hour averaged measurements obtained when the particulate sulfur fluxes were successfully measured. The wind speed u was measured at a 39 m height and $\sigma_\theta \bar{u}$ was found at 42 m.

TABLE IV

Summary of half-hour averaged measurements obtained when the particulate sulfur fluxes were successfully measured. The wind speed u was measured at a 39 m height and $\sigma_\theta \bar{u}$ was found at 42 m.

Date Jan., '81	Time center (EST)	u ($m\ s^{-1}$)	u_* ($cm\ s^{-1}$)	$\sigma_\theta \bar{u}$ ($cm\ s^{-1}$)	$L_w E$ ($W\ m^{-2}$)	H ($W\ m^{-2}$)	T_a (°C)	v_d ozone ($cm\ s^{-1}$)	F_c ($mg\ m^{-2}\ s^{-1}$)	v_d particle ($cm\ s^{-1}$)	v_d part. S ($cm\ s^{-1}$)
26	10:15	4.0	64	94	19	49	9.2	0.35	0.56	0.01	0.07
26	17:45	2.1	26	30	3	−16	15.4	0.03	0.07	0.02	0.27
26	18:15	2.5	28	32	2	−20	14.8	0.07	0.09	0.12	−0.68
26	18:45	2.1	24	30	4	−20	14.3	0.11	0.03	−0.04	0.09
26	19:15	2.4	26	29	4	−18	14.0	0.07	0.05	−0.02	−0.28
26	19:45	2.3	20	28	3	−13	13.4	0.06	0.01	−0.05	−0.30
27	10:15	2.2	28	45	1	31	11.7	–	0.06	−0.01	−0.19
27	10:45	2.5	38	45	0	85	13.2	–	0.54	0.11	−0.03
27	11:45	2.6	38	56	4	56	15.0	–	0.42	0.07	0.30
27	12:45	1.8	25	57	0	26	15.2	0.08	0.36	0.14	−0.83
27	13:15	1.8	34	44	0	11	15.3	0.22	0.36	−0.14	−0.25
28	10:45	3.6	56	196	12	43	7.5	0.17	0.01	0.68	−0.13
28	11:15	3.2	66	308	35	120	7.9	1.33	0.37	–	−0.73
28	11:45	2.7	57	192	37	209	8.4	1.24	0.39	0.32	0.48
28	12:15	2.9	48	316	13	89	8.5	1.24	0.13	0.80	−0.08
28	12:45	3.3	56	125	45	231	9.2	0.41	0.31	0.55	−0.43
28	13:15	2.8	57	63	25	237	9.7	0.27	0.36	0.20	2.48
28	13:45	2.5	36	116	27	220	9.6	0.46	0.42	−0.12	−1.28
28	15:15	1.5	35	72	11	55	9.7	0.25	0.40	0.09	−0.04

from both laboratory and field experiments (Brutsaert, 1979). However, the deposition velocities predicted for particles (near 0.4 μm diameter) are one to three orders of magnitude larger than produced in some recent modeling efforts for vegetative canopies (Davidson and Friedlander, 1978; Slinn, 1982). It seems that the main feature lacking in some models (not Brutsaert's, 1979) is a description of turbulence provided external to the boundary layers of individual surface elements; ambient turbulence levels defined by $\sigma_u/\bar{u}$ can be 10–500 times greater than that found in wind tunnels. Clearly, such external turbulence can greatly increase diffusional transport of scalar quantities such as heat through quasilaminar sublayers (Schlicting, 1968), and this process possibly extends to substances with a very small Brownian or molecular diffusivity in air. There have been only a few cases in which laboratory studies have provided direct support for the relatively large air-surface exchange rates often found in the field. Schuepp's (1982) experiments indicate enhanced deposition to individual coniferous shoots in some special cases of highly agitated flow, and this might be related to the increase in heat and water vapor associated with intermittent flow (e.g., Schuepp, 1980). Sehmel and Hodgson (1978) extrapolate their wind-tunnel observations to cases of large surface roughnesses often found in the field, and empirically predict that the deposition velocities can be rather large even for 0.4 μm diameter particles. While Sehmel and Hodgson do not directly consider turbulence levels or wind direction changes to be important factors, the intensity of microscale wind motions near the surface would certainly be enhanced by increased surface roughness.

At this point it is worth considering the impaction resistance r_3 in Equation (9), heretofore neglected for particulate sulfur. The stopping distance for particles of the relevant size (near 0.4 μm diameter) is quite small, typically 1 μm in wind speeds near 1 m s^{-1} (Chamberlain, 1975). As a result, impaction only occurs well within the viscous boundary layer, from a distance of less than three particle diameters of the actual surface; according to traditional arguments, this should severely limit particle deposition by impaction. This does little to explain the large submicron-particle deposition velocities over a pine forest (Hicks *et al.*, 1982) and above grass (present authors, unpublished); these deposition velocities for fine particles and particulate sulfur are considerably in excess of those predicted by formulae such as Equation (7) that only describe diffusion processes. Perhaps intense turbulence generated by the atmosphere and by individual surface elements, often close to and upwind of others in a dense vegetative canopy, disturbs viscous sublayers to the extent that particles with small stopping or relaxation times can be impacted quite efficiently. Conifer ovulate cones, for example, cause flow disturbances that enhance pollen deposition in the downwind portions of the cones (Niklas and Paw U, 1982). More research is needed to study such effects of locally generated turbulence.

4. Conclusion

The vertical exchanges of ozone, carbon dioxide, and fine particles near 0.1 μm in diameter above a wintertime deciduous forest are controlled by quite diverse surface

processes. Aerodynamic resistances are small (usually 0.1 s cm^{-1} or less) in the top portion of the canopy but are large in the lower portions of the canopy and in the leaf litter and soil beneath. The variations of O_3 fluxes support the latter contention because they are not smaller when the ground is covered with snow, which removes O_3 much more slowly than should leaf litter. In fact, O_3 deposition velocities seem to increase when the snow covers the ground, perhaps because of increased solar irradiation, via reflection, on the twigs and branches above. This, together with the systematic variation of v_d for O_3 ranging from 0.1 cm s^{-1} at night to typically 0.3 cm s^{-1} in sunlit conditions when no snow is present, suggest that solar radiation has an important role, perhaps through producing local warming and associated convective mixing or through photo-activation of receptor sites in the canopy. Carbon dioxide fluxes, directed upward because of respiration at the surface, are strongly temperature dependent, in that the vertical fluxes are very small for temperatures near 0 °C and rise to over 0.8 mg m^2 s^{-1} with air temperatures exceeding 15 °C during the daytime. The role of aerodynamic resistance to and from the leaf litter does not appear to be significant, but might be important in the canopy above.

Fine particles with diameters near 0.1 μm are deposited fairly efficiently in gusty conditions and seem most sensitive to turbulence intensity, especially as related to the magnitude of wind direction fluctuations. Values of deposition velocity are near 0.8 cm s^{-1} in the maximum turbulence levels encountered, but drop off to nearly zero with light winds and stable conditions when turbulence is at a minimum. In a gross highly-averaged sense, the deposition velocities seem to be controlled by diffusion processes. With snow present on the surface beneath the canopy, the fine-particle fluxes are directed upward above the tree canopy, perhaps due to the effects of particle growth in high relative humidities near the surface.

The measurements of particulate sulfur deposition lead to rather inconclusive results. Over 19 half-hour data-collection periods, v_d averaged -0.08 ± 0.18 cm s^{-1}. Some trend with turbulence levels might be present but is not statistically significant. At best, it can be said that for similar values of u_* and atmospheric stability, the deposition velocities seem to be notably less than above a pine plantation during summer.

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References

Allen, L. H. Jr. and Lemon, E. R.: 1976, 'Carbon Dioxide Exchange and Turbulence in a Costa Rican Rain Forest', in J. L. Monteith (ed.), *Vegetation and the Atmosphere*, Vol. 2, *Case Studies*, Academic Press, New York, pp. 265–308.

Barrie, L. A. and Walmsley, J. L.: 1978, 'A Study of Sulphur Dioxide Deposition Velocities to Snow in Northern Canada', *Atmos. Environ.* **12**, 2331–2332.

Brutsaert, W.: 1979, 'Heat and Mass Transfer to and from Surfaces with Dense Vegetation or Similar Permeable "Roughness"', *Boundary-Layer Meteorol.* **16**, 365–388.

Chamberlain, A. C.: 1975, 'The Movement of Particles in Plant Communities', in J. L. Monteith (ed.), *Vegetation and the Atmosphere*, Vol. 1, *Principles*, Academic Press, New York, pp. 155–203.

Davidson, C. I., and Friedlander, S. K.: 1978, 'A Filtration Model for Aerosol Dry Deposition: Application to Trace Metal Deposition from the Atmosphere', *J. Geophys. Res.* **83**, 2343–2352.

Denmead, O. T.: 1976, 'Temperate Cereals', in J. L. Monteith (ed.), *Vegetation and the Atmosphere*, Vol. 2, *Case Studies*, Academic Press, New York, pp. 1–31.

Dovland, H. and Eliassen, A.: 1976, 'Dry Deposition on a Snow Surface', *Atmos. Environ.* **10**, 783–785.

Edwards, N. T.: 1975, 'Effects of Temperature and Moisture on Carbon Dioxide Evolution in a Mixed Deciduous Forest Floor', *Soil Soc. of Amer. Proc.* **39**, 361–365.

Edwards, N. T. and McLaughlin, S. B.: 1979, 'Temperature-Independent Diel Variations of Respiration Rates in Quercus alba and Liriodendron tulipifera', *Oikos* **31**, 200–206.

Friedlander, S. K.: 1977, *Smoke, Dust, and Haze*, John Wiley & Sons, New York.

Galbally, I. E.: 1971, 'Ozone Profiles and Ozone Fluxes in the Atmospheric Surface Layer', *Quart J. Roy. Meteorol. Soc.* **97**, 18–29.

Galbally, I. E. and Roy, C. R.: 1980, 'Destruction of Ozone at the Earth's Surface', *Quart. J. Roy. Meteorol. Soc.* **106**, 599–620.

Garland, J. A. and Cox, L. C.: 1982, 'Deposition of Small Particles to Grass', *Atmos. Environ.* **16**, 2699–2702.

Hicks, B. B., Wesely, M. L., Durham, J. L., and Brown, M. A.: 1982, 'Some Direct Measurements of Atmospheric Sulfur Fluxes over a Pine Plantation', *Atmos. Environ.* **17**, 2899–2903.

Ibrahim, M., Barrie, L. A., and Fanaki, F.: 1983, 'An Experimental and Theoretical Investigation of the Dry Deposition of Particles of Snow, Pine Trees, and Artificial Collectors', *Atmos. Environ.* **17**, 781–783.

Jarvis, P. G., Jarvis, G. B., and Landsberg, J. J.: 1976, 'Coniferous Forest', in J. L. Monteith (ed.), *Vegetation and the Atmosphere*, Vol. 2, *Case Studies*, Academic Press, New York, pp. 171–240.

Lenschow, D. H., Pearson, R. Jr., and Stankov, B. B.: 1982: 'Measurements of Ozone Vertical Flux to Ocean and Forest', *J. Geophys. Res.* **87**, 8827–8832.

McMahon, T. A. and Denison, P. J.: 1979, 'Empirical Atmospheric Deposition Parameters – A Survey', *Atmos. Environ.* **13**, 571–585.

Niklas, K. J. and Paw U, K. T.: 1982, 'Pollination and Airflow Patterns around Conifer Ovulate Cones', *Science* **217**, 442–444.

Schuepp, P. H.: 1980, 'Heat and Moisture Transfer from Flat Surfaces in Intermittent Flow: A Laboratory Study', *Agric. Meteorol.* **22**, 351–366.

Schuepp, P. H.: 1981, 'Laboratory Studies on Dry Deposition of Submicron-Size Particles on Coniferous Foliage', *Boundary-Layer Meteorol.* **24**, 465–480.

Schlicting, H.: 1968, *Boundary-Layer Theory*, McGraw Hill Book Company, New York.

Sehmel, G. A.: 1980, 'Particle and Gas Dry Deposition: A Review', *Atmos. Environ.* **14**, 983–1011.

Slinn, W. G. N.: 1982, 'Predictions for Particle Deposition to Vegetative Canopies', *Atmos. Environ.* **16**, 1785–1794.

Tajchman, S. J.: 1981, 'Comments on Measuring Turbulent Exchange Within and Above Forest Canopy', *Bulletin Amer. Meteorol. Soc.* **62**, 1550–1559.

Webb, E. K., Pearman, G. I., and Leunig, R.: 1980, 'Correction of Flux Measurements for Density Effects due to Heat and Vapor Transfer', *Quart. J. Roy. Meteorol. Soc.* **106**, 85–100.

Wesely, M. L.: 1983, 'Turbulent Transport and Ozone to Surfaces Common in the Eastern Half of the United States', Advan. Sci. Technol. Vol. 12, Wiley, New York, pp. 345–370.
Wesely, M. L. and Hicks, B. B.: 1977, 'Some Factors that Affect the Deposition Rates of Sulfur Dioxide and Similar Gases on Vegetation', *J. Air Pollution Control Assoc.* **27**, 1110–1116.
Wesely, M. L. and Hicks, B. B.: 1979, 'Dry Deposition and Emission of Small Particles at the Surface of the Earth', *Preprint Vol., Fourth Symp. on Turbulence, Diffusion, and Air Pollution*, Jan. 15–18, Reno. NV, Am. Meteorol. Soc., Boston, MA, pp. 510–513.
Wesely, M. L., Hicks, B. B., Dannevik, W. P., Frisella, S., and Husar, R. B.: 1977, 'An Eddy-Correlation Measurement of Particulate Deposition from the Atmosphere', *Atmos. Environ.* **11**, 561–563.
Wesely, M. L., Eastman, J. A., Cook, D. R., and Hicks, B. B.: 1978, 'Daytime Variations of Ozone Eddy Fluxes to Maize', *Boundary-Layer Meteorol.* **15**, 361–373.
Wesely, M. L., Cook, D. R., and Williams, R. M.: 1981, 'Field Measurement of Small Ozone Fluxes to Snow, Wet Bare Soil, and Lake Water', *Boundary-Layer Meteorol.* **20**, 459–471.
Wesely, M. L., Cook, D. R., Hart, R. L., and Williams, R. M.: 1982, 'Air-Sea Exchange of CO_2 and Evidence for Enhanced Upward Fluxes', *J. Geophys. Res.* **87**, 8827–8832.
Whelpdale, D. M. and Shaw, R. W.: 1974, 'Sulphur Dioxide Removal by Turbulent Transfer over Grass, Snow, and Water Surfaces', *Tellus* **26**, 196–204.
Woodwell, G. M. and Dykeman, W. R.: 1966, 'Respiration of a Forest Measured by Carbon Dioxide Accumulation During Temperature Inversions', *Science* **154**, 1031–1034.

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